Auxiliary Table for Computations in Chemical Thermodynamics

by

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taken 273.16, so that 25 degrees Centigrade corresponds to $T = 298.16$).

Further, with the aid of the formula

$$\Delta F^{o} = -RT \ln K$$

the value of the equilibrium constant K can be obtained.

This method of calculation is often called the Ulich approximation method, although essentially this method was used earlier by Lewis and Randal (1).

In many cases, the approximation method suffices, especially if it leads to very high absolute values of ΔF^{o}, which indicate that the reaction can either proceed to completion or that it cannot practically proceed at all.

(b) Exact calculation. If the approximate calculation indicates that both the starting substances and the reaction products are present in noticeable amounts at equilibrium, then an exact calculation can be made. This calculation takes into account the value of ΔC_p and is performed in the following manner.

The values of C_p are expressed by interpolation formulas of the type

$$C_p = G_o + G_1 T + G_2 T^2, \qquad (4)$$

where G_o, G_1, and G_2 are constants. Thus, for ΔC_p, we obtain

$$C_p = \Delta G_o + \Delta G_1 T + \Delta G_2 T^2. \qquad (5)$$

The variation of the heat content ΔH is then expressed by the following equation:

$$H = \Delta H_o + \Delta G_o T + \tfrac{1}{2} \Delta G_1 T^2 + \tfrac{1}{3} \Delta G_2 T^3. \qquad (6)$$

The constant ΔH_o is determined by substituting in this equation the values of ΔH_{298} and $T = 298.16$. Further, the value of ΔF^o for the required temperature is determined from the following equation:

$$\frac{\Delta F^o}{T} = \frac{\Delta H_o}{T} - \Delta G_o \ln T - \frac{1}{2}\Delta G_1 T - \frac{1}{6}\Delta G_2 T^2 + J \qquad (7)$$

Also, the constant J is first determined by substituting in this equation the value of ΔF^o_{298}, which is calculated from the equation

$$\Delta F^o_{298} = \Delta H_{298} - 298.16 \cdot \Delta S^o_{298}. \qquad (8)$$

Sometimes, following Kelly, use is made of the following expressions for the heat capacities

$$C_p = G_o + G_1 T + G_{-2} T^{-2}, \qquad (9)$$

where G_o, G_1, and G_{-2} are constants. The calculation is carried out as described above.

With ΔF^o determined, K is obtained with the aid of equation (3).

The actual performance of the indicated calculation is quite cumbersome and requires much time. In addition, the result of the previously performed approximate calculation is not utilized and all calculations have to be performed from the start.

Below is outlined a method of exact calculation, which eliminates the requirement of calculating the auxiliary magnitudes ΔH_o and J and shortens the calculating operations through use of an auxiliary table which is a development of the table published by Lewis and Randal (1).

The calculation is based on the utilization of the equation

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(10)

It is easy to see that the last member in the right-hand portion of the equation provides a correction for the results obtained by the approximate calculation. If we introduce the criterion

$$M_n = \int_{298}^{T} \frac{dT}{T^2} + \int_{298}^{T} T^n \, dT, \qquad (11)$$

then

$$M_o = \ln \frac{T}{298.16} + \frac{298.16}{T} - 1 \qquad (12)$$

and when $n \neq 0$,

$$M_n = \frac{T^n}{n(n+1)} + \frac{298.16^{n+1}}{(n+1)T} - \frac{298.16^n}{n} \; * \qquad (13)$$

*By rearrangement, the following formulas, more suitable for calculating the magnitudes M_1 and M_{-2} are obtained: $M_1 = \frac{1}{2T}(T - 298.16)^2$; $M_{-2} = \frac{1}{2}(\frac{1}{298.16} - \frac{1}{T})^2$

The table lists the values of M_o, M_1, M_2, and M_{-2} for different temperatures (and also values of $1/T$, which are useful for calculations). The values for intermediate temperatures not listed in the table can be determined by linear interpolation. With the aid of the table it is easy to calculate the magnitude $\Delta F^o/T$ from the formula

$$\frac{\Delta F^o}{T} = \frac{\Delta H_{298}}{T} - \Delta S_{298} - (M_o \Delta G_o + M_1 \Delta G_1 + M_2 \Delta G_2 + M_{-2} \Delta G_{-2}) \qquad (14)$$

Equation (14) is applicable when the heat capacity of a portion of the substances is expressed by equations of type (4) and for the remaining equations of type (9).

Some members of the type $M_n \Delta G_n$ may be absent in exceptional cases. By dividing the calculated value of $\Delta F^o/T$ into 4.5740, we get -log K.

Example: To determine the equilibrium constant of the reaction

$$C_{graphite} + CO_2 = 2CO$$

at 1000 degrees Centigrade. The following data are given:

$C + \frac{1}{2}O_2 = CO;$ $H_{298} = -26,393$ calories

$C + O_2 = CO_2$ $H_{298} = -94,030$ calories

$C;\ S^o_{298} = 1.36$ calories /degree $CO_2;\ S^o_{298} = 51.08$ calories/degree

$$CO;\ S^o_{298} = 47.32 \text{ calories/degree}$$

$$C;\ C_p = 2.673 + 2.617 \times 10^{-3}T - 1.169 \times 10^5 T^{-2} \quad (0\text{-}1100^o\ C)$$

$$CO_2;\ C_p = 6.85 + 8.533 \times 10^{-3}T - 2.475 \times 10^{-6}T^2 \quad (0\text{-}1700^o\ C)$$

$$CO;\ C_p = 6.60 + 1.20 \times 10^{-3}T \quad (0\text{-}2200^o\ C)$$

From the above given data, we obtain for our reaction:

$$\Delta H_{298} = 41,244 \text{ calories}$$

$$\Delta S^o_{298} = 42.20 \text{ calories/degree}$$

$$G_o = 3.677; \quad G_1 = -8.750 \times 10^{-3}; \quad G_2 = 2.475 \times 10^{-6}; \quad G_{2} = 1.169 \times 10^5$$

From the table, we obtain for 1000 degrees Centigrade:

$$1/T = 0.78545 \times 10^{-3}; \quad M_o = 0.6858; \quad M_1 = 0.3733 \times 10^3;$$
$$M_2 = 0.2326 \times 10^6; \quad M_{-2} = 0.3299 \times 10^{-5}$$

Hence, with the aid of equation (14), we get:

$$F^o/T = 41.244\ (0.78545) - 42.20 - 3677\ (0.6858) + 8.75\ (0.3733) - 2.475\ (0.2326) - 1.169\ (0.3299) = -10.02$$

$$\log K = 10.02/4.574 = 2.191$$

The first two items, which correspond to, the approximate calculation on the assumption that $\Delta C_p = 0$, give $\Delta F^o/T = 9.81$ and $\log K = 2.145$. An error of 0.05 in log K obtained by the approximate calculation corresponds to an error of 12 percent in the magnitude K (in other cases it may be considerably larger).

It is easy to understand that the table can be utilized for various other calculations; for example, for calculating the magnitudes ΔS^o_{298} and ΔF^o_{298} from the experimental values of ΔH_{298} and ΔF^o for any desired temperature T (from the magnitude K for this temperature).

We wish to point out still another application of the table. Let us assume that we have the experimental values of K and hence of ΔF^o for various temperatures and the expressions of heat capacities of the reacting substances and that it is required to determine the values of ΔH_{298} and ΔS^o_{298}. Usually, such a problem is solved in the following manner. On the basis of equation (7), we plot 1/T on the abscissa and the magnitude

$$\frac{\Delta F^o}{T} + \Delta G_0 \ln T + \frac{1}{2}\Delta G_1 T + \frac{1}{6}\Delta G_2 T^2$$

along the ordinate and then we draw the best possible straight line through the points corresponding to the experimental data. The slope of the straight line gives the magnitude of ΔH_0 and the section which it cuts off on the ordinate axis gives J.

Further, we calculate ΔH_{298} with the aid of equation (6) and ΔF^o_{298} with the aid of equation (7) and from here we find ΔS^o_{298}.

The same result can be obtained in a much shorter way with the aid of the tabulated values of M_n. We construct a curve by plotting 1/T along the abscissa and $\frac{\Delta F^o}{T} + \sum M_n \Delta G_n$ along the ordinate. Then,

TABLE FOR THERMODYNAMIC CALCULATIONS

t° C	T	$\frac{1}{T}\cdot 10^3$	M_o	$M_1\cdot 10^{-3}$	$M_2\cdot 10^{-6}$	$M_{-2}\cdot 10^5$
0	273.16	3.6609	0.0040	0.0011	0.0003	0.0047
25	298.16	3.3539	0.0000	0.0000	0.0000	0.0000
50	323.16	3.0944	0.0032	0.0010	0.0003	0.0034
100	373.16	2.6798	0.0234	0.0075	0.0024	0.0227
150	423.16	2.3631	0.0547	0.0185	0.0063	0.0491
200	473.16	2.1134	0.0919	0.0324	0.0115	0.0769
250	523.16	1.9115	0.1322	0.0484	0.0180	0.1040
300	573.16	1.7447	0.1737	0.0660	0.0257	0.1295
350	623.16	1.6047	0.2156	0.0848	0.0344	0.1530
400	673.16	1.4855	0.2573	0.1044	0.0422	0.1745
450	723.16	1.3828	0.3006	0.1249	0.0549	0.1943
500	773.16	1.2394	0.3385	0.1459	0.0666	0.2123
550	823.16	1.2148	0.3777	0.1674	0.0792	0.2288
600	873.16	1.1453	0.4160	0.1893	0.0927	0.2439
650	923.16	1.0832	0.4532	0.2116	0.1072	0.2578
700	973.16	1.0275	0.4893	0.2341	0.1225	0.2706
750	1023.16	0.97736	0.5254	0.2569	0.1387	0.2824
800	1073.16	0.93183	0.5586	0.2798	0.1557	0.2933
850	1123.16	0.89034	0.5917	0.3030	0.1737	0.3035
900	1173.16	0.85240	0.6240	0.3263	0.1925	0.3129
950	1223.16	0.81756	0.6552	0.3498	0.2121	0.3216
1000	1273.16	0.78545	0.6858	0.3733	0.2326	0.3299
1050	1323.16	0.75577	0.7155	0.3970	0.2540	0.3375
1100	1373.16	0.72825	0.7444	0.4208	0.2762	0.3447
1150	1423.16	0.70266	0.7725	0.4446	0.2993	0.3514
1200	1473.16	0.67881	0.7999	0.4686	0.3232	0.3578

t^oC	T	$\frac{1}{T}\cdot 10^3$	M_o	$M_1\cdot 10^{-3}$	$M_2\cdot 10^{-6}$	$M_{-2}\cdot 10^5$
1250	1523.16	0.65653	0.8267	0.4926	0.3480	0.3638
1300	1573.16	0.63566	0.8527	0.5167	0.3736	0.3694
1350	1623.16	0.61608	0.8782	0.5408	0.4001	0.3748
1400	1673.16	0.59767	0.9031	0.5650	0.4274	0.3798
1450	1723.16	0.58033	0.9272	0.5892	0.4556	0.3846
1500	1773.16	0.56396	0.9510	0.6135	0.4845	0.3892
1550	1823.16	0.54850	0.9732	0.6378	0.5144	0.3935
1600	1873.16	0.53386	0.9968	0.6622	0.5450	0.3976
1650	1923.16	0.51998	1.0168	0.6865	0.5766	0.4016
1700	1973.16	0.56080	1.0408	0.7110	0.6089	0.4053
1750	2023.16	0.49236	1.0598	0.7354	0.6421	0.4089
1800	2073.16	0.48236	1.0830	0.7599	0.6761	0.4123
1850	2123.16	0.47100	1.1034	0.7844	0.7110	0.4156
1900	2173.16	0.46016	1.1235	0.8089	0.7467	0.4187
1950	2223.16	0.44981	1.1432	0.8334	0.7833	0.4217
2000	2273.16	0.43992	1.1616	0.8580	0.8206	0.4246

the slope of the best possible straight line through the experimental points, in accordance with equation (14), determines the magnitude ΔH_{298} and the section which it cuts off on the ordinate axis is equal to $-\Delta S^0_{298}$.

Along with the above described approximate calculation, which corresponds to the assumption that $\Delta C_p = 0$, Ulich (2) proposed more complex methods of approximate calculation ("second approximation" and "third approximation"). In view of the simplicity of the exact calculation, as described herein, the Ulich methods seem superfluous.

LITERATURE

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2. G. Ulich, Usp. khim., (Progress of Chemistry), 1940, 9, 214.

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